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### (54) THERMOPLASTIC POLYESTER RESIN COMPOSITION

(57)Abstract:

**PROBLEM TO BE SOLVED:** To obtain a thermoplastic polyester resin composition having not only mechanical characteristics and durability but also sufficiently excellent moldability.

**SOLUTION:** This thermoplastic polyester resin composition is obtained by compounding 100 pts.wt. of a thermoplastic polyester resin (A) with 0.1-10 pts.wt. of a carboxylic acid reactive group-containing polymer (B-1) and/or a compound (B-2) containing plural oxazoline groups in the molecule and 0.01-5 pts.wt. of a carboxylic acid anhydride (C). Another thermoplastic polyester resin composition is obtained by melting and kneading 100 pts.wt. of the component A with 0.1-10 pts.wt. of the component (B-1) and/or the component (B-2) and 0.01-5 pts.wt. of the component C. This method for producing thermoplastic polyester resin molding product is a method for producing a molding product comprising the thermoplastic polyester resin as a material and is obtained by molding the thermoplastic polyester resin composition.

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**CLAIMS**

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[Claim(s)]

[Claim 1]In a thermoplastic polyester resin composition which uses thermoplastic polyester resin as an essential ingredient, A compound (B-2) which has two or more oxazoline groups to thermoplastic-polyester-resin (A)100 weight section in a polymer (B-1) which has a carboxylic acid reactivity group of 0.1 - 10 weight section, and/or a molecule, A thermoplastic polyester resin composition which blends a carboxylic anhydride (C) of 0.01 to 5 weight section, and is characterized by things.

[Claim 2]The compound (B-2) 0.1 - ten weight sections which have two or more oxazoline groups in a polymer (B-1) which has thermoplastic-polyester-resin (A)100 weight section and a carboxylic acid reactivity group, and/or a molecule, And a thermoplastic polyester resin composition which carries out melt kneading of the carboxylic anhydride (C) 0.01 - the five weight sections.

[Claim 3]The thermoplastic polyester resin composition according to claim 1 or 2 whose carboxylic acid reactivity groups in said polymer (B-1) are an oxazoline group and/or an epoxy group.

[Claim 4]A thermoplastic polyester resin composition given in either to claims 1-3 which has a number average molecular weight of said polymer (B-1) in the range of 1000-20000.

[Claim 5]A manufacturing method of a thermoplastic-polyester-resin Plastic solid which is the method of manufacturing a Plastic solid made from thermoplastic polyester resin, and is characterized by fabricating using a thermoplastic polyester resin composition of a statement to either to claims 1-4.

[Claim 6]A manufacturing method of the thermoplastic-polyester-resin Plastic solid according to claim 5 in which said shaping is at least one sort chosen from extrusion molding, injection molding, blow molding, foaming, and spinning shaping.

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**DETAILED DESCRIPTION**

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[Detailed Description of the Invention]

[0001]

[Field of the Invention]This invention relates to a thermoplastic polyester resin composition and its directions for use. It is related with the thermoplastic polyester resin composition excellent in the moldability, and its directions for use in more detail.

[0002]

[Description of the Prior Art]The polyalkylene terephthalate represented with thermoplastic polyester resin especially polyethylene terephthalate (PET), and polybutylene terephthalate, Since it has the characteristic which was excellent in many, it is widely used also as a raw material of industrial use textiles, a film, and other Plastic solids, but the more outstanding a mechanical property, heat resistance, hydrolysis resistance, and a moldability are demanded. In order to present blow molding and extrusion molding especially, generally, melt viscosity of polyester resin is too low, drawdown is intense, and it is most difficult to obtain the mold goods of desired shape. Since melting was repeated between recovery operation when recycle employment of the abandonment PET is carried out, intrinsic viscosity (IV) fell, it was not suitable for spinning shaping any longer, and textiles with sufficient intensity and ductility were not able to be obtained. In order to improve these, as a method of it being effective to raise a degree of polymerization and to decrease the terminal carboxyl group in polyester, and denaturalizing polyester for such the purpose, There is a method of using the chain elongation agent which can react to the end group of polyester resin and can extend a polymer chain. For example, the method (JP,55-161823,A) of using a screw oxazoline compound, the method (JP,47-13860,B, JP,2-276820,A, JP,5-506056,A) of using a polyfunctional compound, etc. are examined.

[0003]However, in these methods, although a mechanical property, heat resistance, and hydrolysis resistance can be given to polyester resin to some extent, it is one side and

sufficient performance cannot be given about a moldability. For example, in the method (JP,55-161823,A) of using the aforementioned screw oxazoline compound, a mechanical property and endurance cannot say that it is enough, either, and cannot give still more sufficient melt viscosity to be suitable for various molding methods, and IV. In the method (JP,47-13860,B, JP,2-276820,A, JP,5-506056,A) of using the aforementioned polyfunctional compound. When too sufficient melt viscosity and IV cannot be given when a polyfunctional epoxy compound, a polyfunctional isocyanate, etc. are used, but it applies to extrusion molding, injection molding, and blow molding, When there was a fault that detailed foam uniform [ since the molecular weight is not enough, when there is a fault that resin will carry out drawdown and it applies to foaming ] since resin viscosity is low is not obtained and it applied to spinning shaping, there was a fault that the thread breakage in spinning happened. If the addition of those compounds is increased in order to raise melt viscosity, a constituent gels and it is known that a moldability will worsen remarkably. These polyfunctional compounds vaporized in the forming cycle, metallic mold contamination was caused, and there were problems, such as spoiling the appearance of mold goods.

[0004]

[Problem(s) to be Solved by the Invention]Therefore, the issue which this invention tends to solve is providing the thermoplastic polyester resin composition which it not only excels in a mechanical property and endurance, but has the fully outstanding moldability.

[0005]

[Means for Solving the Problem]this invention person inquired wholeheartedly that an aforementioned problem should be solved. As a result, with a carboxylic anhydride to thermoplastic polyester resin further, A constituent obtained by blending a compound which has a specific basis into a specific reactant group content polymer and/or a molecule could solve an aforementioned problem, and found out that it was suitably [ for various forming processes ] applicable. This invention was carried out in this way, and was completed.

[0006]Namely, a thermoplastic polyester resin composition concerning this invention, In a thermoplastic polyester resin composition which uses thermoplastic polyester resin as an essential ingredient, A compound (B-2) which has two or more oxazoline groups to thermoplastic-polyester-resin (A)100 weight section in a polymer (B-1) which has a carboxylic acid reactivity group of 0.1 - 10 weight section, and/or a molecule, A carboxylic anhydride (C) of 0.01 to 5 weight section is blended.

[0007]Another thermoplastic polyester resin composition concerning this invention, thermoplastic polyester resin -- (-- A --) -- 100 -- a weight section -- carboxylic acid -- reactivity -- a group -- having -- a polymer (B-1) -- and/or -- a molecule -- inside -- plurality -- oxazoline -- a group -- having -- a compound (B-2) -- 0.1 - ten -- a weight section -- and -- a carboxylic anhydride -- (-- C --) -- 0.01 - five -- a weight section -- melt kneading -- carrying out --

becoming .

[0008]A manufacturing method of a thermoplastic-polyester-resin Plastic solid concerning this invention is a method of manufacturing a Plastic solid made from thermoplastic polyester resin, and fabricates using a thermoplastic polyester resin composition of this invention.

[0009]

[Embodiment of the Invention]Hereafter, this invention is explained in detail.

(Constituent) The thermoplastic polyester resin composition concerning this invention, In the thermoplastic polyester resin composition which uses thermoplastic polyester resin as an essential ingredient, The compound (B-2) which has two or more oxazoline groups to thermoplastic-polyester-resin (A)100 weight section in the polymer (B-1) which has a carboxylic acid reactivity group of 0.1 - 10 weight section, and/or a molecule, The carboxylic anhydride (C) of 0.01 to 5 weight section is blended.

[0010]Another thermoplastic polyester resin composition concerning this invention, thermoplastic polyester resin -- (-- A --) -- 100 -- a weight section -- carboxylic acid -- reactivity -- a group -- having -- a polymer (B-1) -- and/or -- a molecule -- inside -- plurality -- oxazoline -- a group -- having -- a compound (B-2) -- 0.1 - ten -- a weight section -- and -- a carboxylic anhydride -- (-- C --) -- 0.01 - five -- a weight section -- melt kneading -- carrying out -- becoming .

[0011]Hereafter, the resin composition concerning these this inventions is explained first. As thermoplastic polyester resin (A) used in this invention, Terephthalic acid, isophthalic acid, naphthalene dicarboxylic acid, diphenyl ether dicarboxylic acid, Succinic acid, adipic acid, sebacic acid, cyclohexanedicarboxylic acid, The polyester which consists of acid components, such as hydroxybenzoic acid, and glycol components, such as ethylene glycol, a trimethylene glycol, tetramethylene glycol, hexamethylene glycol, and cyclohexane dimethanol, is mentioned. Copolymerization of the ingredients of three or more organic functions other than the two above-mentioned functional constituent, such as trimellitic acid and pentaerythritol, may be carried out. The polyester derived from oxy acid and those residue, such as p-oxybenzoic acid, The polyether ester which consists of residue of aromatic ether dicarboxylic acid, such as polylactone, such as poly PIPARO lactone, and 1,2-bis(4,4-dicarboxy methylphenoxy)ethane, and the above-mentioned glycol component, The copolyester etc. which combined the dicarboxylic acid, oxy acid, and glycols etc. which were furthermore stated above can be mentioned. The block copolymerized polyester to which coupling of two or more sorts of low-molecular-weight polyester was carried out using 2 functional chain elongation agent can be mentioned.

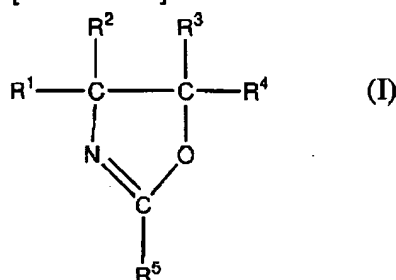
[0012]Polyethylene terephthalate and polybutylene terephthalate are preferred in these polyester. It was obtained from fabrication operation or after-use abandonment, for example, abandonment PET of the gestalt of a film, a sheet, textiles, bottle mold goods, etc. can also be

used. The polymer (B-1) which has a carboxylic acid reactivity group which can be used in this invention refers to the polymer which has a functional group which can react to carboxylic acid. Here, although an oxazoline group and an epoxy group are mentioned, the functional group which can react to carboxylic acid is an oxazoline group preferably, for example, in order to fully demonstrate the effect of this invention. At least one sort of said functional group which it has in a polymer (B-1) may be two or more sorts.

[0013]When a polymer (B-1) has an oxazoline group, it is general formula (I).

[0014]

[Formula 1]



[0015]the inside of a formula,  $R^1$ ,  $R^2$ ,  $R^3$ , and  $R^4$  -- respectively -- independent -- hydrogen.

They are halogen, alkyl, an aralkyl, phenyl, or substituted phenyl,  $R^5$  is an un-annular organic group with an addition condensation nature unsaturated bond. It is a polymer which polymerizes at least one sort of other monomers (b-2) the addition condensation nature oxazoline compound (b-1) expressed and if needed and which has two or more oxazoline groups as a side chain.

[0016]As an example of said addition condensation nature oxazoline compound (b-1), For example, 2-vinyl-2-oxazoline, 5-methyl-2-vinyl-2-oxazoline, 4,4-dimethyl- 2-vinyl-2-oxazoline, 4,4-dimethyl- 2-vinyl-5,5-dihydro-4H-1,3-oxazine, Although vinyl oxazoline, such as 4,4,6-trimethyl 2-vinyl-5,6-dihydro-4H-1,3-oxazine, 2-isopropenyl-2-oxazoline, and 4,4-dimethyl- 2-isopropenyl-2-oxazoline, is mentioned, it is not limited to in particular these. Also in a monomer which has these oxazoline group, since [ for acquisition / that 2-isopropenyl-2-oxazoline is easy and ] reactivity is good, it is desirable.

[0017]Although the amount in particular of addition condensation nature oxazoline compound (b-1) used is not limited, it is desirable among an oxazoline group content polymer that it is [ 0.5 % of the weight or more ] less than 50 % of the weight. Less than 0.5% of the weight of quantity of a moldability and a heat-resistant improved effect is insufficient, and even if it uses it 50% of the weight or more, an effect does not change but is economically disadvantageous.

[0018]A monomer (b-2) besides the above does not react to an oxazoline group, but if it is addition condensation nature oxazoline (b-1) and a copolymerizable monomer, There is no restriction in particular and For example, methyl acrylate (meta), butyl acrylate (meta), (meta-)

acrylic ester [, such as 2-ethylhexyl acrylate, ] (meta-); (meta-) -- unsaturated nitrile [, such as acrylonitrile, ]; (meta-) -- acrylamide. Unsaturated amide, such as N-methylol(metha)acrylamide; Vinyl acetate, Vinyl ester, such as vinyl propionate; The methyl vinyl ether, Vinyl ether, such as ethyl vinyl ether; Alpha olefin; VCM/PVC, such as ethylene and propylene, Halogen-containing [, such as vinylidene chloride, vinyl, fluoridation, ] alpha and beta-unsaturated monomers; alpha, such as styrene and alpha-methylstyrene, and beta-unsaturation aromatic monomers are mentioned, and one sort or two sorts or more of these mixtures can be used.

[0019]When a polymer (B-1) has an epoxy group, it is a polymer which polymerizes the same monomers (b-2) of other as at least one sort of above-mentioned a monomer (b-3) which has an epoxy group, and if needed and which has two or more epoxy groups as a side chain. As an example of a monomer (b-3) of having said epoxy group, For example, glycidyl ester species of unsaturation organic acid, such as metaglycidyl acrylate, glycidyl methacrylate, glycidyl ethacrylate, and itaconic acid glycidyl; although glycidylethers, such as allyl glycidyl ether, etc. are mentioned, it is not limited in particular. Also in these, metaglycidyl acrylate and glycidyl methacrylate are preferred.

[0020]A polymer (B-1), for example An addition condensation nature oxazoline compound (b-1) and/or an epoxy group content monomer (b-3), And a monomer component which consists of at least one sort of other monomers (b-2) if needed can be conventionally manufactured by the publicly known polymerizing method, for example, a solution polymerization method, suspension polymerization method, emulsion polymerization method, a bulk polymerization method, etc. In measurement of GPC (gel permeation chromatography), a number average molecular weight of a polymer (B-1) which has a carboxylic acid reactivity group used in this invention has the preferred range of 1000-20000, and especially its range of 1500-10000 is preferred. Since the molecular weight of a constituent of this invention in which a number average molecular weight is obtained by less than 1000 is not enough, even if there is a tendency for a moldability to worsen, and a heat-resistant improved effect moreover also tends to decrease and it exceeds 20000, it is in a tendency for the moldability of a constituent of this invention obtained to be inferior.

[0021]Although a supplying form in particular of a polymer (B-1) is not restricted, a field of handling to a solid or an organic solvent solution is preferred, and especially a solid is preferred. With a compound (B-2) which can be used in this invention and which has two or more oxazoline groups in a molecule. For example, a 1,3-phenylenescrew (2-oxazoline), a 1,4-phenylenescrew (2-oxazoline), A 2,2-screw (2-oxazoline), a 2,2-screw (4-methyl-2-oxazoline), A 2,2-screw (4,4-dimethyl- 2-oxazoline), a 2,2-screw (4-ethyl-2-oxazoline), A 2,2-screw (4,4-diethyl- 2-oxazoline), a 2,2-screw (4-propyl-2-oxazoline), A 2,2-screw (4-butyl-2-oxazoline), a 2,2-screw (4-hexyl-2-oxazoline), A 2,2-screw (4-phenyl-2-oxazoline), a 2,2-screw (4-

cyclohexyl-2-oxazoline), A 2,2-screw (4-benzyl-2-oxazoline), a 2,2-ethylene screw (2-oxazoline), 2,2-tetramethylene bis (2-oxazoline), 2,2-hexa methylenebis (2-oxazoline), 2,2-octa methylenebis (2-oxazoline), a 2,2-ethylene screw (4-ethyl-2-oxazoline), Although screw oxazoline compounds, such as a 2,2-tetraethylene screw (4-ethyl-2-oxazoline) and a 2,2-cyclohexylenescrew (4-ethyl-2-oxazoline), are mentioned, a 1,3-phenylenescrew (2-oxazoline) is mentioned preferably.

[0022]A carboxylic anhydride (C) used in this invention has most preferred dianhydride, especially pyromellitic dianhydride of aromatic tetracarboxylic acid, for example. As other useful carboxylic anhydrides, for example 3,3',4,4'-diphenyltetracarboxylic acid, (Perylene 3,4,9,10) Tetracarboxylic acid, 3,3',4,4'-benzophenone tetracarboxylic acid, 2,2-bis(3,4-dicarboxyphenyl)propane, bis(3,4-dicarboxyphenyl)ether, Anhydrides, such as a bis(3,4-dicarboxyphenyl)sulfone, 1,2,3,4-cyclobutane tetracarboxylic acid and a 2,3,4,5-tetracarboxyhydronaliumfranc, phthalic acid, and maleic acid, are mentioned.

[0023]A carboxylic anhydride (C) may be a polymer, for example, may be a copolymer of styrene and a maleic anhydride. One gestalt of a thermoplastic polyester resin composition of this invention, A compound (B-2) which it has two or more oxazoline groups to thermoplastic-polyester-resin (A)100 weight section in a polymer (B-1) which has a carboxylic acid reactivity group, and/or a molecule 0.1 - 10 weight section, A carboxylic anhydride (C) is a gestalt which it comes to blend at a rate of 0.01 - 5 weight section. This gestalt Resin (A), a polymer (B-1), and/or a compound (B-2), And may be a gestalt contained in the state of a mixture without an acid anhydride (C) reacting mutually, and. It may be in a state to which a part of each ingredient reacted, i.e., a gestalt which a mixture and a reactant coexist and is contained, or each ingredient may be a gestalt contained as a reactant which reacted thoroughly.

[0024]A gestalt of another thermoplastic polyester resin composition of this invention, The compound (B-2) 0.1 - ten weight sections which have two or more oxazoline groups in a polymer (B-1) which has thermoplastic-polyester-resin (A)100 weight section and a carboxylic acid reactivity group, and/or a molecule, And it is a gestalt which carries out melt kneading of the carboxylic anhydride (C) 0.01 - the five weight sections. In this gestalt, resin (A), a polymer (B-1), and/or a compound (B-2), And a resin composition in which at least some acid anhydrides (C) react by melt kneading, and this specific reaction gestalt be passed is not only excellent in a mechanical property and endurance, but has the fully outstanding moldability preferably especially. Once pelletizing melt kneading of each of this ingredient using one axis or a biaxial extrusion machine, shaping may be presented with it and shaping may be promptly presented with it after melt kneading. Melt kneading treatment of said each ingredient may be carried out at once, or each ingredient may be kneaded independently, it may mix later, or melt kneading of each ingredient may be added and carried out in 2 steps or more.

[0025]If there are few loadings of a polymer (B-1) and/or a compound (B-2) than 0.1 weight



sections, a moldability and a heat-resistant improved effect will not be demonstrated, but if more than ten weight sections, a problem of physical properties falling will occur. Loadings of a polymer (B-1) and/or a compound (B-2) are 0.1 to 7 weight section, and are 0.2 to 5 weight section more preferably. If there are few loadings of a carboxylic anhydride (C) than 0.01 weight sections, a moldability improved effect will not be demonstrated, but if more than five weight sections, sufficient moldability improved effect will not be acquired, and also it will have an adverse effect on the physical properties of mold goods. Loadings of a carboxylic anhydride (C) are 0.1 - the amount part of duplexs further more preferably 0.05 to 3 weight section more preferably 0.01 to 3 weight section.

[0026]Under the present circumstances, the range of carboxyl group =0.1 in the oxazoline group / polyester resin in a carboxylic acid reactivity group in a polymer (B-1) which has a carboxylic acid reactivity group, and/or a compound (B-2) - 3 (mole ratio) is preferred. Unless the physical properties of a polyester resin composition obtained are furthermore spoiled in this invention, a raw material (A), At the time of combination of (B-1) and/or (B-2), and (C), at the time of shaping. Polyolefines, vinyl chloride resin, such as other additive agents, for example, polyethylene, polypropylene, and polybutylene, A polyvinyl acetal, polyvinyl alcohol, polystyrene, an AS resin, Other thermoplastics, such as ABS plastics, polyamide, polycarbonate, and thermoplastic elastomer, Bulking agents, such as paints, a color, a reinforcement, calcium carbonate, and talc, a heat-resistant improver, an oxidation degradation inhibitor, a plasticizer, a weather resistance improver, lubricant, a release agent, a nucleus agent, a crystal accelerator, a fluidity improving agent, a spray for preventing static electricity, stabilizer, fire retardant, etc. may be added. Although an addition in particular is not limited, it is 0 - 30 weight section more preferably zero to 50 weight section to polyester resin (A)100 weight section.

[0027]When polyolefine is included as the above-mentioned additive agent etc., although polyethylene, polypropylene, polybutylenes, those copolymers, those mixtures, etc. are mentioned, specifically, Preferably, it is polyethylene, polypropylene, those copolymers, or those mixtures, and is polypropylene still more preferably. A desirable molecular weight of the above-mentioned polyolefine of within the limits of 5000-1 million is a thing of 10000-100000 within the limits still more preferably. Per polyester resin 100 above-mentioned weight section and the above-mentioned polyolefine of an addition of the above-mentioned polyolefine are within the limits of 0.2 - the amount part of duplexs still more preferably 0.1 to 5 weight section more preferably 0.05 to 10 weight section.

[0028]Glass fiber, an aramid fiber, carbon fiber, etc. are mentioned, also especially in inside, it is a technique well used depending on a use, for example, it is [ blending a fiber reinforced as a reinforcement has preferred glass fiber, and ] chopped glass fiber more preferably. Although not limited especially as an addition of a fiber reinforced, in the case of glass fiber, 5 to 50 % of

the weight is preferred to polyester resin, and 10 to 45% is still more preferred. In the case of an aramid fiber and carbon fiber, 2 to 50 % of the weight is preferred, and it is still more preferred. [ of 5 to 45 % of the weight ] If the length of textiles is usually used length, there will be no restriction in particular, but it is 0.2-4 mm still more preferably 0.1-5 mm preferably.

[0029]Especially as the combination methods, such as other additive agents, it is not limited by a compound (B-2), a carboxylic anhydride (C), and necessity of having two or more oxazoline groups, into polyester resin (A), a polymer (B-1) which has a carboxylic acid reactivity group, and/or a molecule. A thermoplastic polyester resin composition of this invention, Blend a compound (B-2) and a carboxylic anhydride (C) which have two or more oxazoline groups into polyester resin (A), a polymer (B-1) which has a carboxylic acid reactivity group, and/or a molecule, and since, As compared with the conventional thermoplastic polyester resin composition, it has the outstanding moldability. A terminal carboxyl group, end hydroxyl in which polyester resin (A) has this, A carboxylic acid reactivity group in a polymer (B-1), an oxazoline group in a compound (B-2), and an acid anhydride group of a carboxylic anhydride (C) carry out a certain reaction or interaction, and it as a result, For example, it is presumed since having long chain branching etc. is a polymer which has the molecular structure which can contribute to an outstanding moldability. On the other hand, if a process condition was not precisely controlled when epoxy compounds, such as bisphenol female mold glycidyl ether, etc. were used, gelling was often caused.

(Use) It is a very desirable mode to use it for various forming processes as mentioned above, since a thermoplastic polyester resin composition of this invention is excellent in a moldability, and to manufacture a Plastic solid made from thermoplastic polyester resin. That is, a manufacturing method of a thermoplastic-polyester-resin Plastic solid of this invention is a method of manufacturing a Plastic solid made from thermoplastic polyester resin, and fabricates using a thermoplastic polyester resin composition of this invention.

[0030]As for said shaping, it is preferred that it is at least one sort chosen from extrusion molding, injection molding, blow molding, foaming, and spinning shaping. A thermoplastic polyester resin composition of this invention, Since the moldability is fully conventionally excellent compared with elegance, mold goods where showed a moldability good for drawdown of resin not happening in particular in the case of extrusion molding and blow molding, and uniform detailed foam was obtained on the occasion of foaming and which were excellent in mechanical properties and appearance with these forming processes are obtained. In spinning shaping, thread breakage becomes difficult to happen.

[0031]Although a making machine in particular used with these shaping is not limited, the usual injection molding machine, what is called an injection-compression-molding machine, a twin screw extruder, a 1 axis screw extruder, a twin screw extruder with a vent, a 1 axis screw extruder with a vent, etc. are used preferably, for example. In the case of extrusion molding, it

can fabricate by a usual method with an extrusion machine usually used. That is, it is fabricated by fusing a constituent of this invention with an extrusion machine, and extruding it more nearly continuously than a die of desired shape by a sheet, film, etc.

[0032]In the case of injection molding, an injection molding machine usually used is used, and it can fabricate it by a usual method. That is, a constituent of this invention can be fused within an extrusion machine, a constituent by which melting was carried out into a metallic mold from a cylinder can be ejected, and a Plastic solid by which size enlargement was carried out to desired shape can be acquired. In the case of blow molding, a blow molding machine generally used for blow molding of thermoplastics is used, and it should just perform it by a usual method. Namely, a thermoplastic polyester resin composition of this invention is plasticized with an extrusion machine etc., this -- an annular die -- extrusion -- or it ejects, annular melting or softened intermediate parison is formed, cooling solidification of the gas is blown, swollen and carried out to a metallic mold inside on both sides of this, and it is fabricated as a hollow body. a gas blown into an inside -- air, nitrogen, and others -- although anything may be used, air is usually used from a field of economical efficiency, and the blow pressure has preferred 3 - 10 kg/cm<sup>2</sup>. It can also fabricate with special blow molding machines, such as a three-dimensional blow molding machine. It is also possible to make a constituent of this invention into one or more layers, and to consider it as a multilayer blow molded article combining a layer by other materials.

[0033]In the case of foaming, melting mixing of a constituent, a thickener, etc. of this invention which adjusted loadings can be carried out within an extrusion machine, for example, and it can fabricate by extruding a mixture obtained by mixing the molten mixture with a foaming agent under high voltage to low-pressure areas in the atmosphere etc. When extruding press machines, such as a single screw extruder, a multi-screw extruder, and a tandem extrusion machine, can be used and it uses these extrusion machines as an extrusion machine which can be used by foaming, for example, said molten mixture is extruded by low-pressure area from a cap.

[0034]As said foaming agent, a physical foaming agent etc. which have the character to evaporate thru/or expand with heating can be used. As an example of this foaming agent, for example Inactive gas; methane, such as carbon dioxide and nitrogen gas, Ethane, normal butane, isobutane, normal pentane, isopentane, A neopentane, normal hexane, 2-methylpentane, 3-methylpentane, Saturated aliphatic hydrocarbon, such as 2,2-dimethylbutane and 2,3-dimethylbutane; Methylcyclopropane, Aromatic hydrocarbon, such as saturation alicycle fellows hydrocarbon; benzene, such as cyclopentane, an ethylcyclobutane, and 1,1,2-trimethyl cyclopropane; Trichloromonofluoromethane, Dichlorofluoromethane, monochlorodifluoromethane, trichlorofluoroethane, Halogenated hydrocarbon, such as dichlorotetrafluoroethane; ketone, such as ether; acetone, such as wood ether and 2-

ethoxyethanol, methyl ethyl ketone, and an acetylacetone, etc. are mentioned, and these are independent, or can mix and use two or more sorts.

[0035]In order that the amount of said foaming agent used may have the expansion ratio of a request of a Plastic solid acquired, In order to be one or more copies preferably and to keep the dimensional stability of a Plastic solid from falling by 0.5 or more weight sections to said molten mixture 100 weight section at the time of extrusion molding, it is more preferred that ten or less weight sections are preferred, and consider it as 7.5 weight sections to said molten mixture 100 weight section.

[0036]In order to make air bubbles fine on the occasion of foaming, it is preferred to add a foaming nucleating additive. As a foaming nucleating additive, talc, silica, kaolin, clay, calcium carbonate, Fatty acid metal salt, such as mineral matter, such as aluminum sulfate, barium stearate, and calcium stearate, AZOJI carvone amide, azobis isobutyldinitrile, AZOJI carbamic acid amide, benzenesulphonyl hydrazide, etc. which are the organic compounds by which it is generated by heating inorganic gas, such as carbon dioxide and nitrogen, are illustrated. As for a foaming nucleating additive, it is preferred to carry out 0.01-5 weight-section addition to resin composition 100 weight section of this invention. When carrying out foaming, in order to improve a moldability, a publicly known reaction accelerator can also be used. For example, they are metallic compounds of I, such as sodium carbonate, II, and III fellows, organic metallic compounds, such as aluminum stearate, etc. The addition is a range with 0.01 to 5 weight section preferred to resin composition 100 weight section of this invention.

[0037]When obtaining polyester fiber with spinning shaping, a spinning process condition of a conventional method can be adopted, but as a spinning speed, it is a part for 1500-4000-m/more preferably by 1500-5000-m/by 1000-6000-m/. Even if it rolls round a line of thread by which melt spinning was carried out as it is, the 1st heated roll once takes over, Even if it extends between the 2nd heated roll and rolls round after heat setting (what is called spinning direct extension), once cooling below to glass transition temperature of polymer on a spinning line, it may roll round after through and heating extension to a non-contact hot tube.

[0038]

[Example]Although this invention is explained concretely below, this invention is not limited to these examples.

(Molecular weight) The number average molecular weight of the polymer was measured with gel permeation chromatography (GPC).

(Intrinsic viscosity (IV)) It measured at 25 \*\* using phenol and the mixed solvent of 6:4 (weight ratio) of tetrachloroethane.

[0039](Evaluation of a moldability)

Foaming nature: O Expansion ratio is 20 or more times.

\*\* expansion ratio exceeds 10 times and they are less than 20 times.

x Expansion ratio is 10 or less times.

Blow-molding nature: O drawdown does not occur but thick uniform mold goods are obtained.

The tear at the time of \*\* entrainment may take place.

The tear at the time of x drawdown or an entrainment takes place.

Injection-molding nature: O Surface appearance fitness.

x -- there is flapping a little.

Spinning moldability: There is no O thread breakage and good.

x thread breakage occurs frequently.

[0040][Reference example 1] 665 copies of toluene was taught to the flask provided with an agitator, the reflux condenser, the nitrogen introducing pipe, the thermometer, and the dropping funnel, and it heated at 90 \*\*, passing nitrogen gas gently. There, the mixture which consists of 512 copies of styrene, 128 copies of 2-isopropenyl-2-oxazoline, and par butyl O (made by Nippon Oil & Fats Co., Ltd.) 25 copy was dropped over 2 hours. After completing a reaction for stirring continuously [ 90 \*\* / for 6 hours ], it cooled to the room temperature and the resin solution was obtained. Next, after moving the obtained resin solution to the rotating evaporator and distilling off toluene by a predetermined temperature and pressure, the residue was ground and the oxazoline group content polymer (B-1a) was obtained. By the IR spectrum, when  $1655\text{-cm}^{-1}$  had characteristic absorption, it checked that an oxazoline group existed in a polymer (B-1a).

[0041]It was 6000 when the number average molecular weight of the obtained oxazoline group content polymer (B-1a) was measured in GPC.

[Reference example 2] Except having replaced said 2-isopropenyl-2-oxazoline with glycidyl methacrylate, it carried out like the reference example 1 and the epoxy group content polymer (B-1b) was obtained. By the IR spectrum, when  $910\text{-cm}^{-1}$  had characteristic absorption, it checked that an epoxy group existed in a polymer (B-1b).

[0042]It was 6000 when the number average molecular weight of the obtained epoxy group content polymer (B-1b) was measured in GPC.

[Examples 1-4 and the comparative examples 1-5] -- thermoplastic-polyester-resin PET-1 (the Kanebo make.) Trade name : Pel bed PBK-1, an oxazoline group content polymer (B-1a), An epoxy group content polymer (B-1b), 1,3-phenylenescrew oxazoline. (It may abbreviate to Ox compound hereafter), bisphenol female mold glycidyl ether. (It may abbreviate to Ep compound hereafter), pyromellitic acid 2 anhydride. After supplying and carrying out melt kneading of at least one sort chosen from (abbreviating to PMDA hereafter) to a biaxial extrusion machine by the blending ratio (weight section) shown in Table 1, it cooled and the resin composition pellet was prepared by the SUTARANDO cutter. The result of having measured IV of the pellet produced by carrying out melt kneading was shown in Table 1.

[0043]In Examples 1-4 and the comparative examples 1-4, Using the obtained resin

composition pellet, with a blow molding machine (Placo Make, S-45ND). The average thickness of 2.5 mm and the cylindrical hollow container of 500 cc of inner capacity were fabricated by the die (diameter [ of 50 mm ] of dice, 3 mm of dice intervals) temperature of 270 \*\*, the die temperature of 80 \*\*, and blow pressure 5 kg/cm<sup>2</sup>, and they estimated blow molding nature. The evaluation result was shown in Table 1.

[0044]In Examples 3-4 and the comparative examples 1-4, the obtained resin composition pellet was introduced into the injection molding machine (the Sumitomo Heavy Industries, Ltd. make, SG25-HIPRO MI1), it fabricated with the nozzle temperature of 280 \*\*, the barrel temperature of 280 \*\*, and 70% of a filling pressure, and injection-molding nature was evaluated. The evaluation result was shown in Table 1. The molecular weight of the bisphenol female mold glycidyl ether used by the comparative example 5 is less than 1000. It is manufactured without passing through what is called a polymerization reaction by a manufacturing process, and does not correspond to the polymer (B-1) said to this invention.

[0045]

[Table 1]

		実施例				比較例				
		1	2	3	4	1	2	3	4	5
配合 / 重 量 部	PET-1	100	100	100	100	100	100	100	100	100
	B-1a	1	2				1			
	B-1b			1				1		
	Ox化合物				1					
	Ep化合物									1
	PMDA	0.5	0.5	0.5	0.5				0.5	0.5
IV (dl/g)		1.0	1.3	0.88	0.92	0.65	0.75	0.69	0.70	測定 不能
フロー成形性		○	○	○	○	×	△	×	×	—
射出成形性		—	—	○	○	×	○	×	×	—

[0046][Examples 5-8 and the comparative examples 6-10] -- thermoplastic-polyester-resin PET-1 (the Kanebo make.) Trade name : Pel bed PBK-1, an oxazoline group content polymer (B-1a), An epoxy group content polymer (B-1b), 1,3-phenylenescrew oxazoline. (It may

abbreviate to Ox compound hereafter), bisphenol female mold glycidyl ether. (It may abbreviate to Ep compound hereafter), pyromellitic acid 2 anhydride. At least one sort chosen from (abbreviating to PMDA hereafter), And talc is mixed with a tumbler as a foaming nucleating additive by the blending ratio (weight section) shown in Table 2, It supplied to the extrusion machine hopper, melting mixing was carried out, the foaming agent (isopentane) of four weight sections was poured in into the molten mixture from the extrusion machine middle, from the nozzle metallic mold, the shape of a rod was made to carry out extrusion foaming into the atmosphere, it cooled, and foam was fabricated. The preset temperature of each part of an extrusion machine was adjusted within the limits of feed zone:268-280 \*\*, compression zone:285-290 \*\*, fusion zone:274-283 \*\*, head section:280-290 \*\*, and metallic mold:265-270 \*\*. The foaming nature of the acquired Plastic solid was evaluated. The evaluation result was shown in Table 2.

[0047]The molecular weight of the bisphenol female mold glycidyl ether used by the comparative example 10 is less than 1000.

It is manufactured without passing through what is called a polymerization reaction by a manufacturing process, and does not correspond to the polymer (B-1) said to this invention.

[0048]

[Table 2]

		実施例				比較例				
		5	6	7	8	6	7	8	9	10
配合 / 重 量 部	PET-1	100	100	100	100	100	100	100	100	100
	B-1a	1	2				1			
	B-1b			1				1		
	Ox化合物				1					
	Ep化合物									1
	PMDA	0.5	0.5	0.5	0.5				0.5	0.5
	タルク	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6
	イソペンタン	4	4	4	4	4	4	4	4	4
発泡成形性		○	○	○	○	×	△	×	×	—

[0049][Examples 9-12 and comparative examples 11-15] Thermoplastic-polyester-resin PET-2 (PET pellet collected from PET film shaping waste), An oxazoline group content polymer (B-1a), an epoxy group content polymer (B-1b), 1,3-phenylenescrew oxazoline (it may abbreviate

to Ox compound hereafter), At least one sort chosen from bisphenol F type epoxy resin (it may abbreviate to Ep compound hereafter) and pyromellitic acid 2 anhydride (it may abbreviate to PMDA hereafter) was supplied to the biaxial extrusion machine with a vent by the blending ratio (weight section) shown in Table 3, and was fused at the barrel temperature of 280 \*\*. Melt spinning was carried out with the conventional method using the melt after melting extrusion, and it rolled round by a part for nozzle temperature [ of 280 \*\* ], and coiling speed/of 5000 m. The melt in front of spinning was taken out, the result of having measured the IV was shown in Table 3, and the evaluation result of spinning nature was also further shown in Table 3.

[0050]The molecular weight of the bisphenol female mold glycidyl ether used by the comparative example 15 is less than 1000.

It is manufactured without passing through what is called a polymerization reaction by a manufacturing process, and does not correspond to the polymer (B-1) said to this invention.

[0051]

[Table 3]

		実施例				比較例				
		9	10	11	12	11	12	13	14	15
配合 / 重 量 部	PET-2	100	100	100	100	100	100	100	100	100
	B-1a	1	2				1			
	B-1b			1				1		
	Ox化合物				1					
	Ep化合物									1
	PMDA	0.3	0.3	0.3	0.3				0.5	0.5
IV (dl/g)		0.60	0.65	0.58	0.60	0.50	0.50	0.48	0.51	0.53
紡糸成形性		○	○	○	○	×	×	×	×	×

[0052]

[Effect of the Invention]According to this invention, the thermoplastic polyester resin composition which it not only excels in a mechanical property and endurance, but has the fully outstanding moldability can be provided. Especially the thermoplastic polyester resin composition of this invention has a high molecular weight and IV, and can also give intensity, such as toughness. A moldability specifically good for the drawdown of resin not happening in



the case of extrusion molding or blow molding is shown, and uniform detailed foam is obtained in the case of foaming. Since stickiness and toughness are given to resin, it is hard to generate the tear of the mold goods in the case of blow molding, etc. In spinning shaping, the problem of the thread breakage becomes difficult to arise.

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[Translation done.]